

# Comparison of the Carbon Bond and SAPRC photochemical mechanisms under conditions relevant to southeast Texas

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## Predictions of SAPRC and CB-IV in Houston's Highly Reactive Industrial Source Region

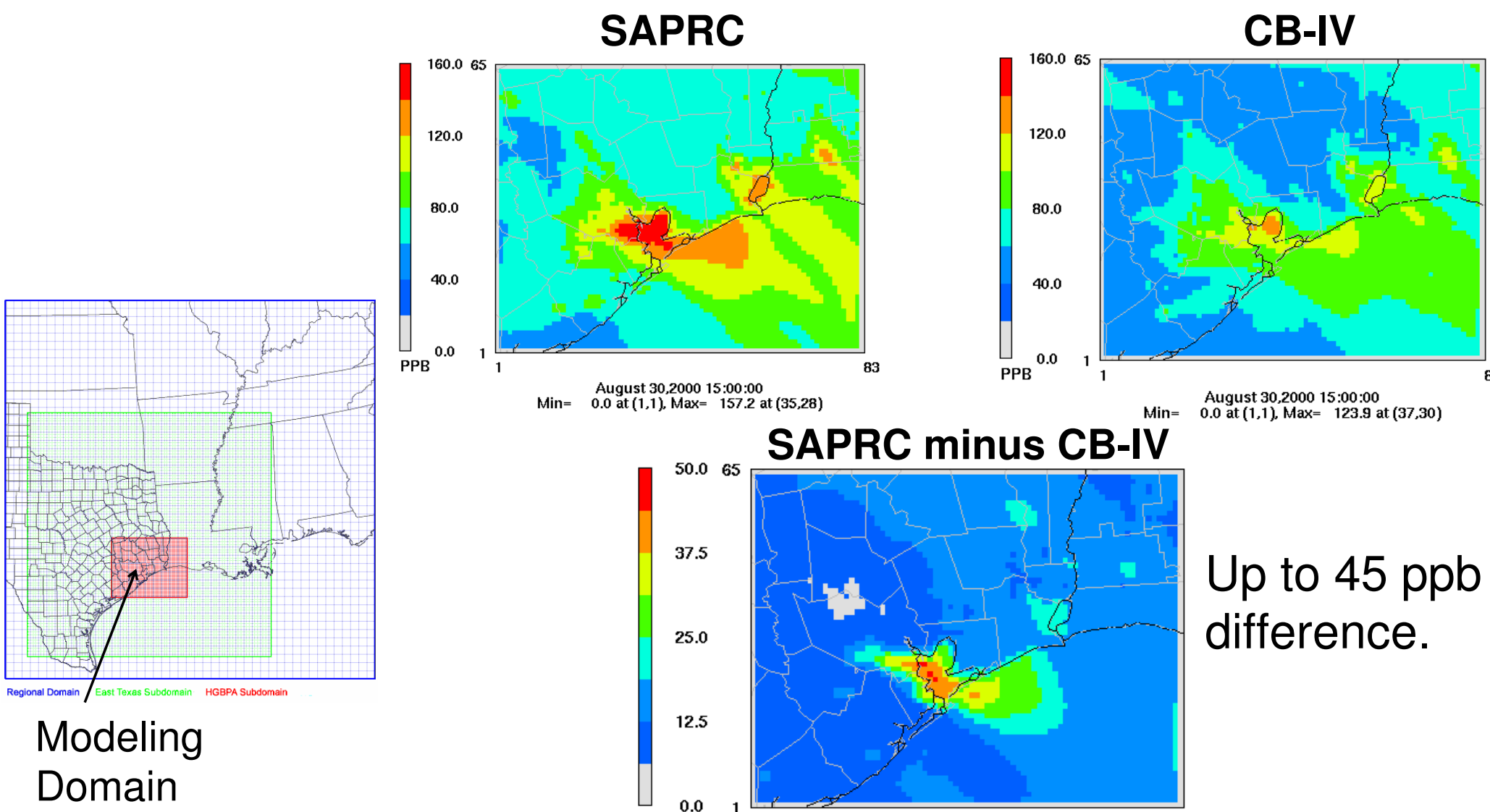
### SAPRC

- Developed by Carter<sup>1</sup> (1990) at the Statewide Air Pollution Research Center.
- Used to quantify reactivities for VOCs for California Air Resources Board (CARB).

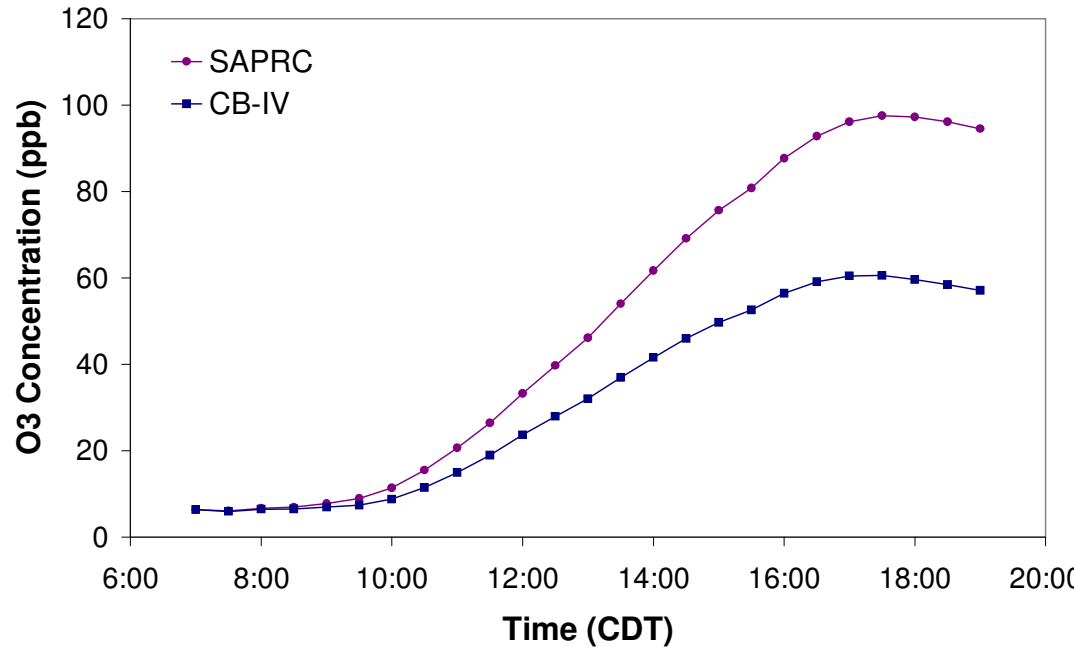
### Carbon Bond (CB) (Gery<sup>2</sup> *et al.*, 1989)

- Widely used in models of regional air quality for regulatory applications.

### Domain-wide maximum ozone concentrations in CAMx on August 30, 2000



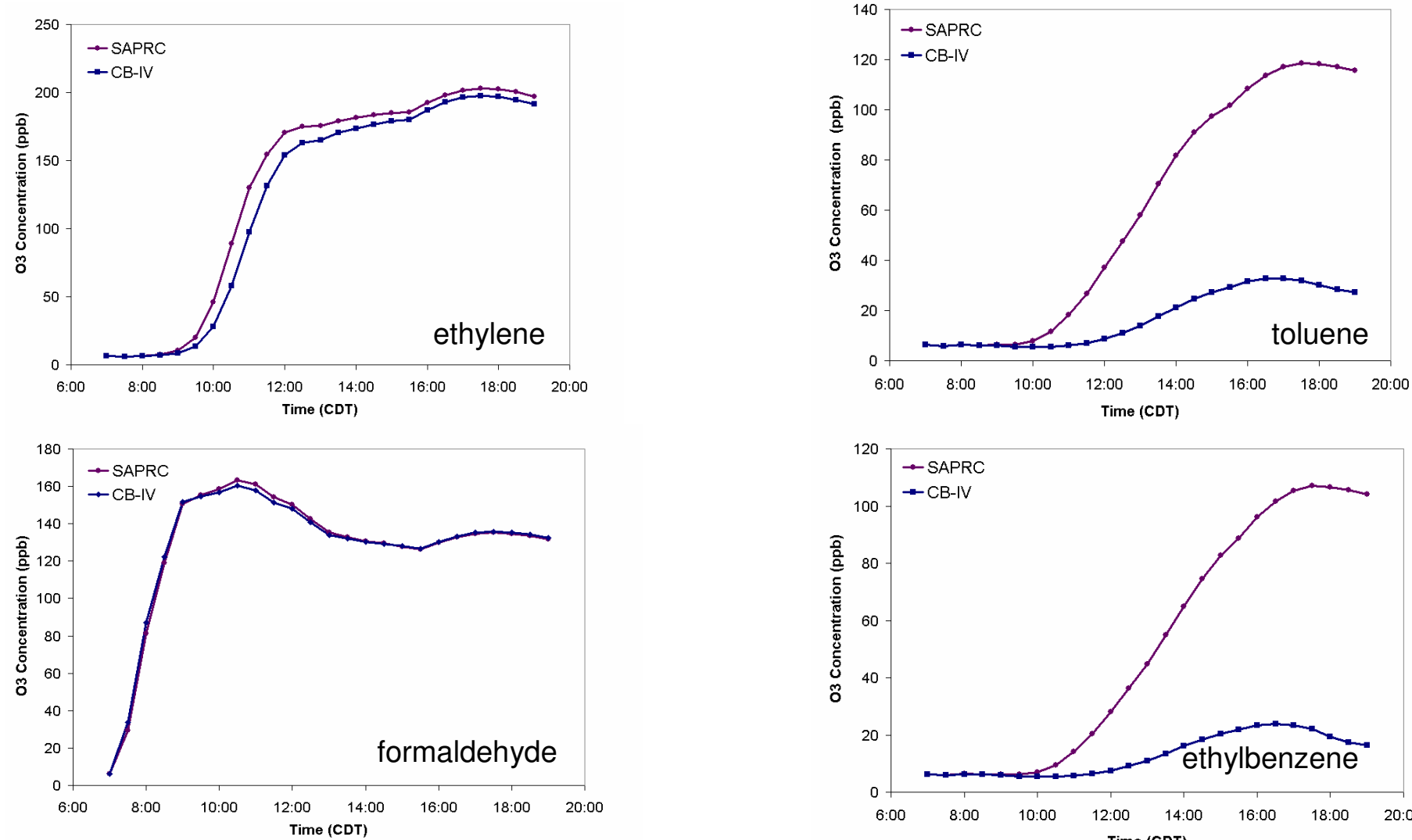
### Differences between SAPRC and CB-IV in box model under conditions of Houston's industrial source region



Conducted sensitivity studies to identify specific hydrocarbons contributing to differences.

- Composition of VOCs emitted into the box replaced with a single chemical species.
- Sensitivity studies not representative of actual atmospheric conditions.

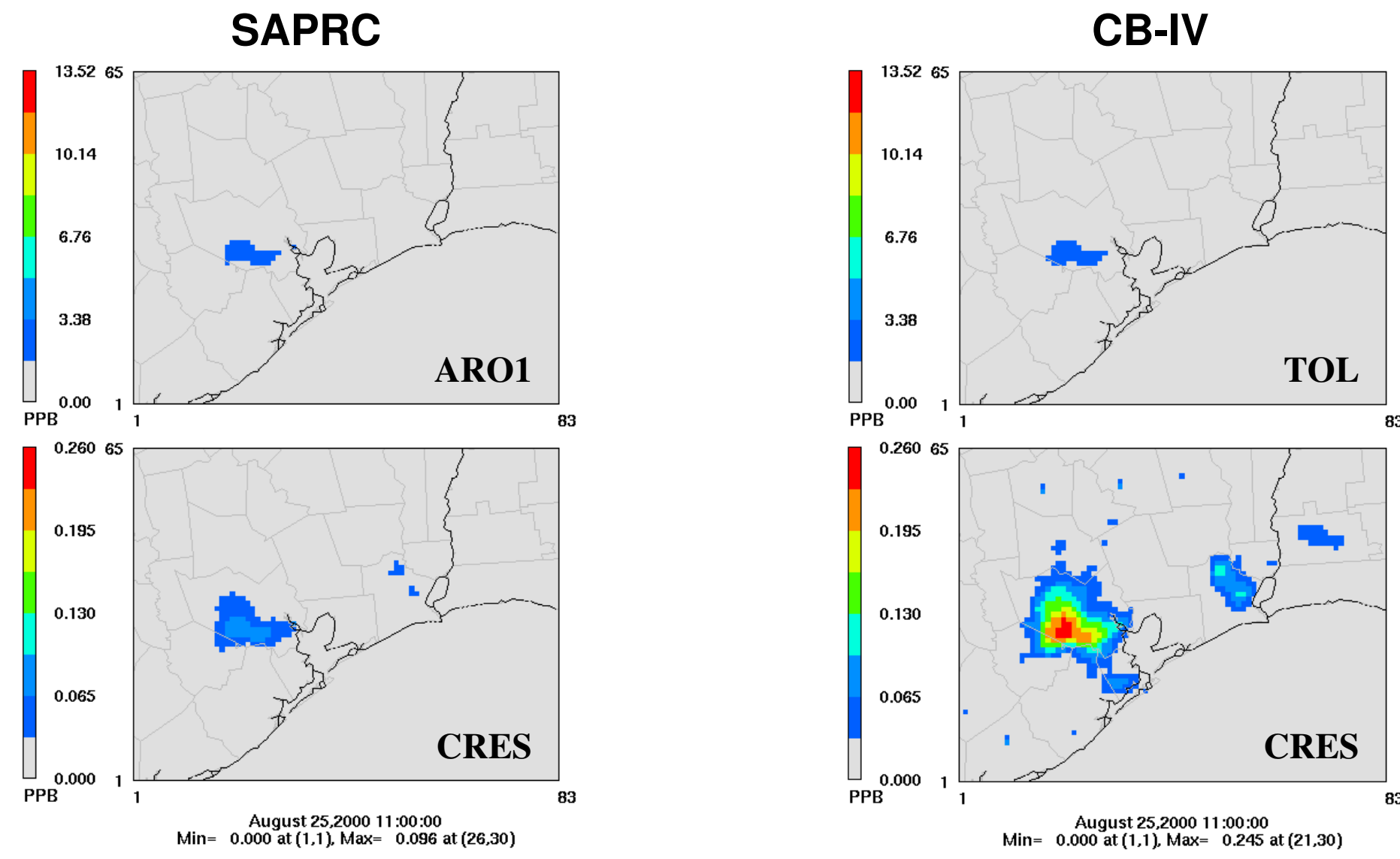
### Ozone predictions in box model when VOC emissions assumed to be single explicitly-modeled species vs. mono-substituted aromatics



Significant discrepancies between mechanisms for aromatics.

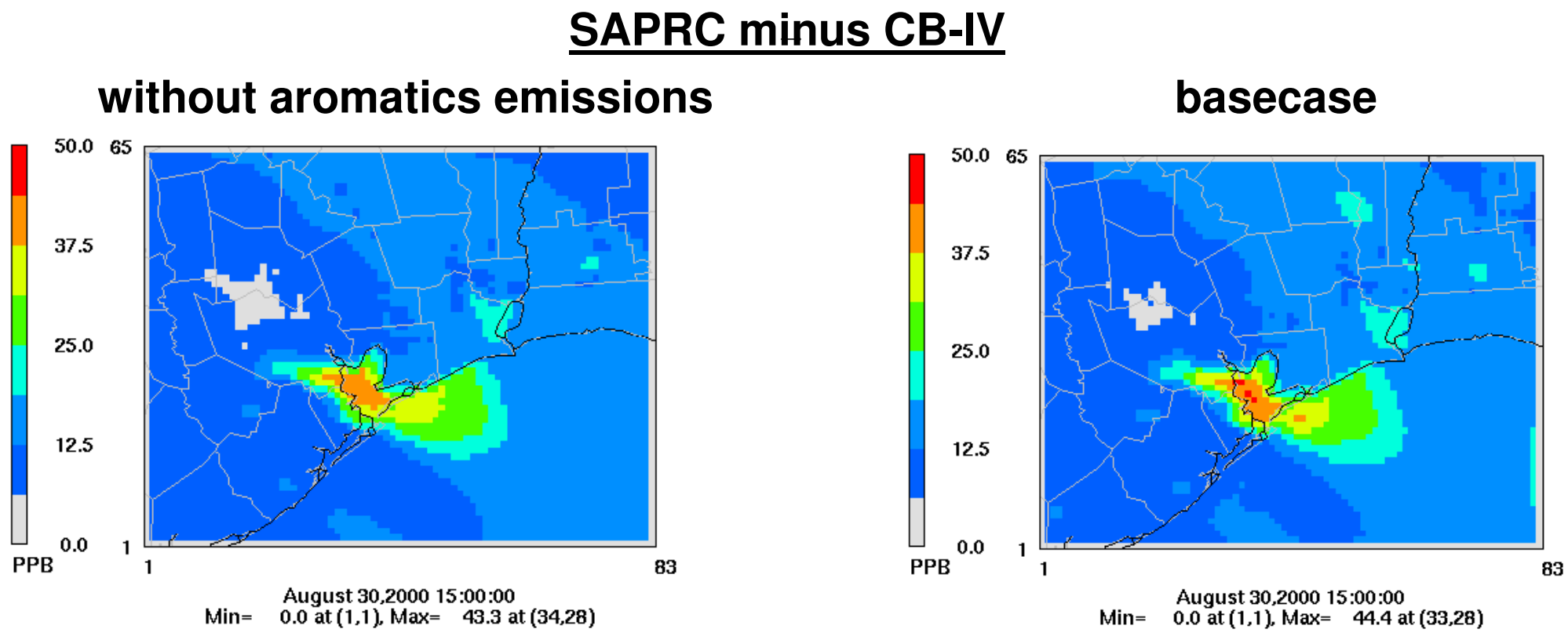
## Aromatics Oxidation

### Different predictions of cresols for consistent mono-substituted aromatics inventories



SAPRC predicts higher ratios of ring-opening to ring-retaining products relative to CB-IV which lead to more free radicals in SAPRC.

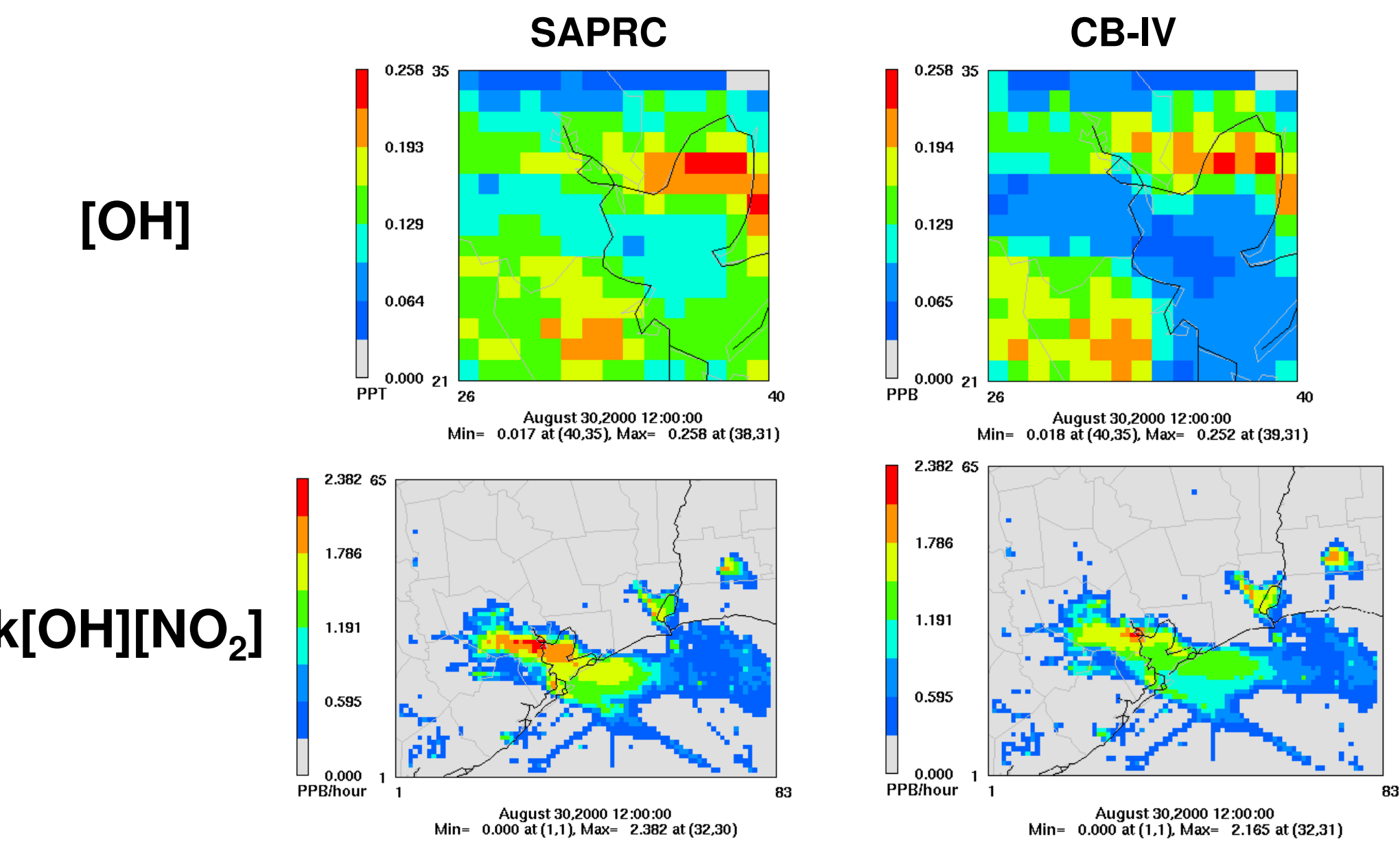
Hypothesis: If aromatics chemistry explains entire difference between mechanisms, eliminating aromatics should cause mechanisms to converge.



Even after eliminating all aromatics emissions, large differences in ozone persist between mechanisms, suggesting that additional causes of differences are also important.

## Free Radical Chemistry

### Predictions of hydroxyl radical concentrations and termination rates

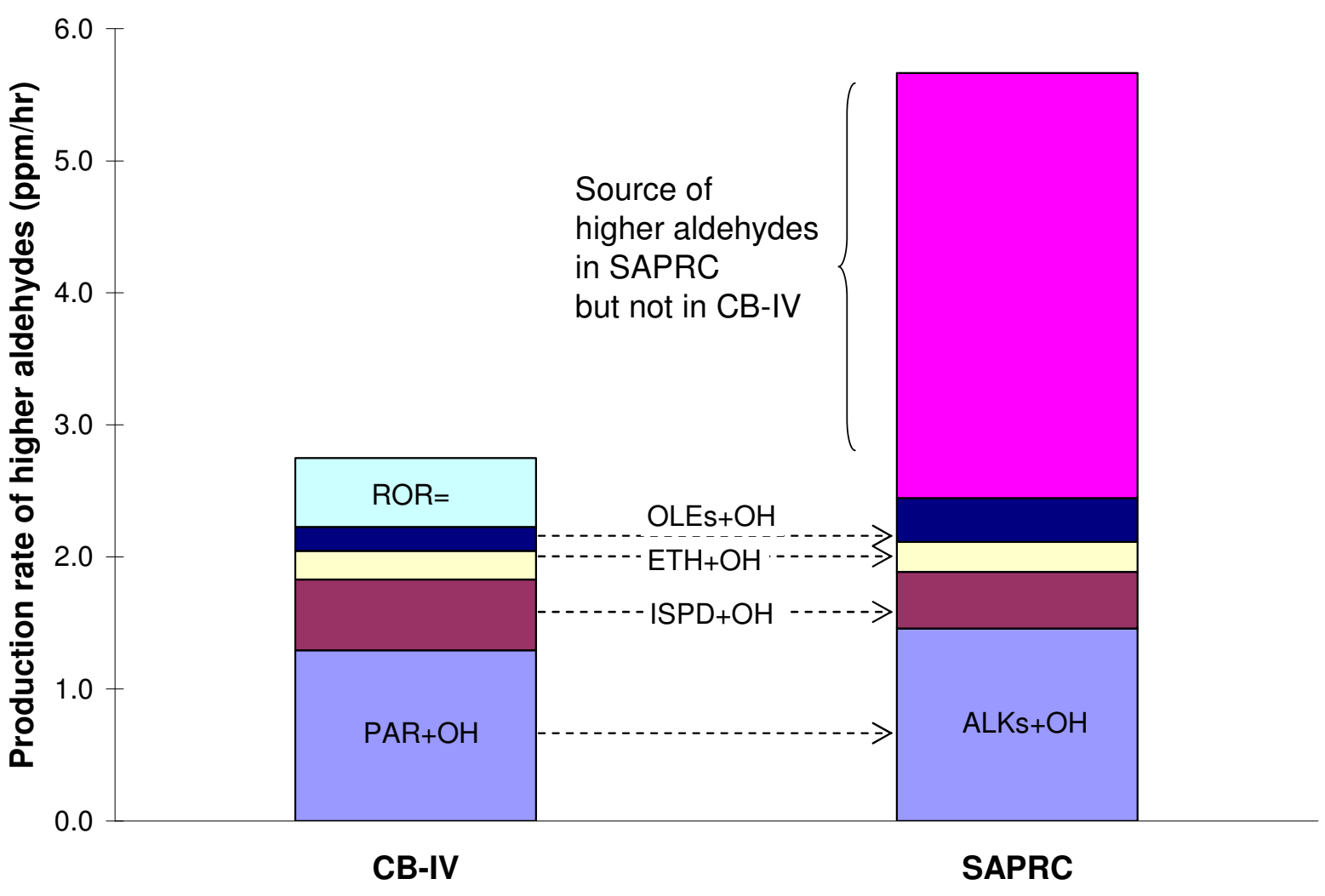


- Higher prediction of hydroxyl radical concentrations in SAPRC relative to CB-IV.
- Higher termination rate of hydroxyl radicals in SAPRC relative to CB-IV.  
→ Higher formation rate of hydroxyl radicals in SAPRC relative to CB-IV.

## Higher Aldehydes Formation

- Since photolysis of aldehydes is a dominant pathway of radical formation, explored differences in the chemistry of aldehydes between SAPRC and CB-IV.

### Relative production of higher aldehydes in SAPRC and CB-IV at location of maximum difference in ozone



Dominant sources of higher aldehydes in SAPRC but not in CB-IV:

- higher aldehydes + OH
- higher peroxyacyl radicals + NO
- higher reactivity non-aldehyde oxygenates + OH
- organic nitrates + OH
- methyl vinyl ketone + OH
- aromatic ring-opening products + OH

## Summary

- Differences of up to 45 ppb in ozone concentrations between SAPRC and CB-IV under Houston-Galveston conditions.
- Differences due to complex and interacting phenomena:
  - Aromatics oxidation.
  - Radical termination and generation.

### References

- Carter, W.P.L.; A detailed mechanism for the gas-phase atmospheric reactions of organic compounds; *Atmos. Environ.* 1990, 24, 481-518.
- Gery, M.W.; Whitten, G.Z.; Killus, J.P.; Dodge, M.C.; A photochemical kinetics mechanism for urban and regional scale computer modeling; *J. Geophys. Res.* 1989, 94, 12925-12956.
- Texas Air Quality Study, II; <http://www.utexas.edu/research/ccer/texaqsII/>.